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Ultrasonic velocity studies in aqueous lithium salts

G Rajarajan, P Revathy and T K Nambinarayanan*
Raman School of Physics, Pondicherry University,
Pondicherry-605 014, India

E-mail : tknambi@yahoo.com

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Abstract : The effect of electrolytes *viz* lithium acetate and lithium chloride, on the temperature of sound velocity maximum of water, has been studied by ultrasonic velocity method. Ultrasonic velocity measurements are carried out in aqueous lithium acetate and lithium chloride in the concentration range 0.1–0.5 molar between 303K and 353K with 10K increment in the temperature. The results are discussed in terms of structure breaking effect of acetate and chloride ions, which changes the temperature velocity maximum of water and on the basis of flickering cluster model of liquid water.

Keywords Ultrosonic velocity, flickering-cluster model, lithium salts

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Our earlier ultrasonic velocity studies [1, 2] in aqueous electrolyte solutions of ammonium chloride, ammonium dihydrogen phosphate and ammonium oxalate at temperature 303K and in di-hydrogen phosphates of sodium and potassium at temperatures 303K, 313K and 323K, showed nonlinear increase in the velocity with concentration and it is attributed to the increased cohesion among the water molecules due to the addition of electrolytes. Lower charge density anions (of relatively high compressibility) contribute more to the increasing rates of conversion between the structural forms of water. Water unlike many other liquids, exhibits anomalies in its physical properties as a function of temperature, such as maximum sound velocity at 348K, maximum density at 276.98K, maximum specific acoustic impedance at 329.4K and minimum adiabatic compressibility at 337K. This peculiarity has been attributed to its hydrogen-bonded structure. This behaviour of water gets modified on addition on electrolytes and also at various temperatures showing a temperature velocity maximum [3-7].

When a solute either electrolyte or non-electrolyte or both, is added to water, it affects the structural equilibrium existing between hydrogen-bonded clusters and monomers. Electrolytes dissolving in water have been classified as structure makers or breakers, depending on whether the existing structural equilibrium of water shifts to the hydrogen-bonded clusters or to the denser monomers. It has been reported that the ions with a low charge density termed as net structure breakers and the ions with a higher charge density termed as net structure makers [8, 9]. Present work is undertaken in order to understand these aspects more vividly and also to study the temperature velocity maximum effect of water in the presence of lithium acetate and lithium chloride in the temperature between 303K and 353K.

All the chemicals used in the present study are of AR grade and are used as such without further purification. Solutions of aqueous lithium acetate and lithium chloride in the concentration range 0.1–0.5 molar are prepared by dissolving known amounts of salt in the double distilled water. The ultrasonic velocity has been measured at a frequency of 10MHz using an ultrasonic time intervalometer (UTI-101). The accuracy in measurement of velocity is $\pm$ 0.01ms^{-1}. The density of the solutions is measured using a specific gravity bottle. The temperatures of the solutions are maintained at the desired temperature with an accuracy of $\pm$0.02K in an electronically controlled thermostatic water bath.

The measured and computed parameters *viz.* density, ultrasonic velocity and adiabatic compressibility for aqueous lithium acetate and lithium chloride are given in Tables 1 and 2. The variation of ultrasonic velocity with temperature is

*Corresponding Author.

Table 1. Ultrasonic velocity and other parameters for aqueous lithium acetate

T K	c molar	ρ kgm^{-3}	u ms^{-1}	β_s x10^{-10} N^{-1}m^2
303	0	998.49	1510.00	4.392
	0.1	1019 69	1513.14	4.183
	0 2	1020 00	1534.00	4 166
	0 3	1021 60	1537 56	4.140
	0 4	1022.89	1542 00	4 111
	0 5	1028 79	1543 92	4 077
313	0	996 24	1526 64	4 306
	0 1	1017 28	1532 07	4 187
	0 2	1019 12	1537 79	4 419
	0 3	1020 84	1545.55	4 101
	0 4	1021 68	1553.92	4.053
	0.5	1025 44	1557.79	4 018
323	0	995 39	1540.04	4.235
	0 1	1015 38	1542.07	4 141
	0.2	1018.24	1543.52	4 122
	0 3	1019 54	1549 58	4 084
	0 4	1020 18	1555 69	4 050
	0 5	1023.67	1562 08	4.003
333	0	992 48	1556 04	4 161
	0 1	1012 19	1567 15	4 022
	0 2	1014 78	1570.69	3 994
	0 3	1016 49	1575.81	3 961
	0 4	1019 29	1582 01	3 919
	0.5	1021.89	1588 13	3 879
343	0	988.44	1561 01	4 151
	0 1	1009 84	1577 99	3 976
	0 2	1011 24	1579 51	3.963
	0 3	1013 42	1585 49	3 625
	0.4	1015 98	1591 02	3.888
	0.5	1017.08	1592 13	3 878
353	0	984.24	1558 99	4.180
	0.1	1004 92	1584.94	3.961
	0.2	1006 20	1591 76	3 922
	0.3	1009.24	1594 66	3 896
	0.4	1012.56	1597 15	3.871
	0.5	1014.39	1598.95	3.855

T = temperature, c = concentration, ρ = density, u = ultrasonic velocity, β_s = adiabatic compressibility

Table 2. Ultrasonic velocity and other parameters for aqueous lithium chloride.

T K	c molar	ρ kgm^{-3}	u ms^{-1}	β_s x10^{-10} N^{-1}m^2
303	0	998.49	1510.00	4.392
	0.1	1014.50	1521.14	4.260
	0 2	1016.59	1530 40	4.199
	0.3	1017.39	1531.54	4.190
	0.4	1019 50	1532 74	4 175
	0 5	1020 04	1535 38	4 185
313	0	996 24	1526.64	4 306
	0 1	1012 49	1532 17	4.207
	0 2	1014.24	1534 69	4 186
	0 3	1015 41	1536 87	4.169
	0 4	1016 92	1538 25	4 155
	0 5	1019 18	1539 41	4 140
323	0	995 39	1540 04	4.235
	0.1	1009.82	1541 29	4.168
	0 2	1011 79	1547 01	4 129
	0 3	1012 91	1551 33	4 102
	0 4	1015 08	1556 69	4.065
	0 5	1016.98	1560 77	4 036
333	0	992 48	1556.04	4 161
	0 1	1007.24	1562 26	4 067
	0 2	1009 68	1565 18	4 042
	0 3	1010.62	1575.81	3 984
	0 4	1012 68	1575 93	3 976
	0 5	1014 24	1577 87	3 960
343	0	988.44	1561 01	4 151
	0.1	1005 08	1573 64	4 017
	0 2	1006.91	1579.33	3.981
	0.3	1008.24	1584.88	3.948
	0 4	1010 34	1585.86	3 935
	0 5	1012 68	1591 20	3 900
353	0	984 24	1558 99	4 180
	0 1	1003.68	1580.00	3 991
	0.2	1004 48	1585.24	3.961
	0 3	1006.74	1591.02	3 924
	0 4	1008.61	1592.87	3.907
	0.5	1010.28	1594.26	3 984

T = temperature; c = concentration; ρ = density, u = ultrasonic velocity, β_s = adiabatic compressibility

graphically represented in Figures 1 and 2 for aqueous lithium acetate and lithium chloride.

It can be seen from the figures that the ultrasonic velocity increases nonlinearly with increase in the concentration of lithium acetate and lithium chloride. The ultrasonic velocity increases with increase in the temperature of the solution from 303K – 353K. The density decreases as the temperature of the solutions increases. For pure water, the ultrasonic velocity increases up to 343K and decreases at 353K. This is in conformation with the earlier studies [10].

The ultrasonic velocity shows a non-linear variation (Figures 1 and 2) for aqueous lithium acetate and lithium chloride as the concentration increases from 0.1 molar to 0.5 molar. However, it can be observed that lithium acetate attains more convexity than lithium chloride. The variation of velocity is high for lithium acetate compared to lithium chloride in the initial temperatures and more or less same in the higher temperatures and also the convexity deviates.

From Figures 1 and 2, the slope value of du/dt is found to be increasing as the concentration of lithium acetate and lithium

chloride is increased. As the temperature increases, the increase in velocity is pronounced in 343K and 353K compared to other temperatures. This is because of the anomalous behaviour of pure water with the addition of lithium acetate and lithium chloride.

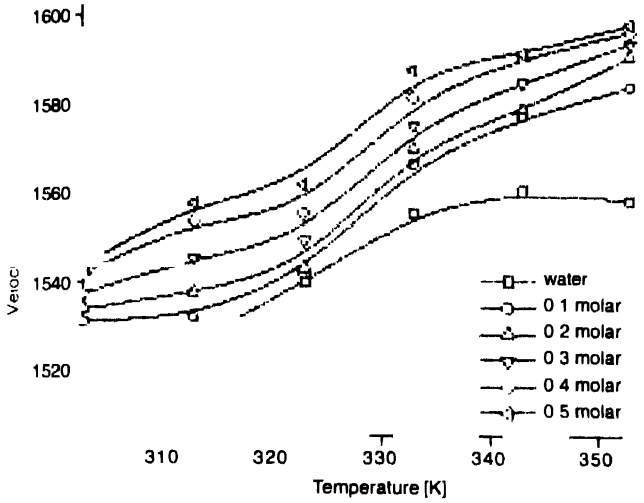

Figure 1. Variation of ultrasonic velocity with temperature for aqueous lithium acetate.

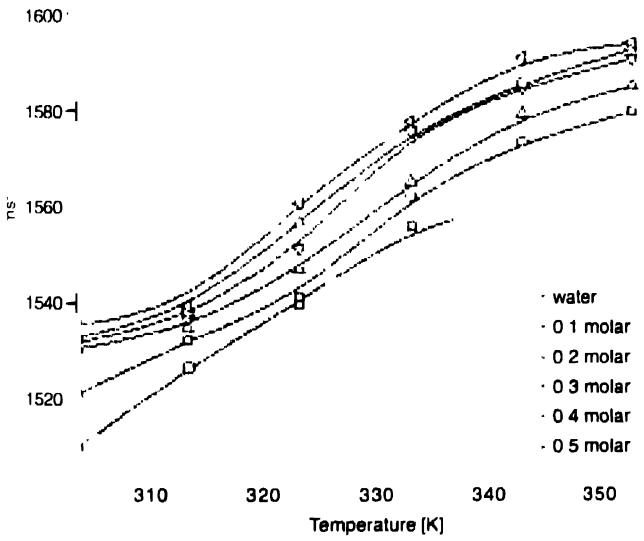

Figure 2. Variation of ultrasonic velocity with temperature for aqueous lithium chloride.

From Figures 1 and 2, it can be seen that the ultrasonic velocity increases (or the adiabatic compressibility decreases) nonlinearly with increasing concentration of the electrolyte throughout the temperature range studied. This can be explained by resorting to Flickering Cluster model of water [11, 12]. According to this model, the water is supposed to consist of hydrogen-bonded clusters and unbonded water molecules. The molecules in the interior of the clusters are quadruply bonded (ice-like) and unbonded water molecules are supposed to occupy the space in between the clusters. The clusters are sometimes referred as 'open structure' water and the dense monomeric fluid is referred to as 'closed structure' water. The mixture is a dynamic mixture and the break down of clusters is a cooperative process. When one hydrogen bond breaks in the cluster, the whole cluster breaks down resulting of an increase in the close packed structure of water. When the electrolytes are dissolved in water, it splits them into lithium ion, acetate and chloride ions, whose net structure-breaking property would first disturb the open structure of water thereby increasing free monomer population, an action that would be followed by structural reorganization leaving the molecules in closely fitted helical cavities [13]. Such an increase in the closed packed structure of water results in increased cohesion of water molecules leading to an increase in the ultrasonic velocity.

When an electrolyte is added to water, some water molecules get arranged around each ion due to their large dipole moment. This interaction between the ion and the surrounding molecules is termed as hydration. The first layer of firmly bound and highly incompressible water molecules forms the primary hydration. The water molecules that surround the primary hydrated molecules form the secondary hydration [14]. Lithium ion because of its strong structure promoting nature [5,15] and high charge density not only polarizes, immobilizes and electrostricts nearest water molecules, but also induces additional order beyond the first layer. One can thus expect that the compressibility of the lithium salt solution decreases as the concentration increases, which increases the velocity of the solution.

When a strong electrolyte is added to water, an electrostatic field is developed by the presence of ions and exerts an electrostrictive effect on the surrounding water molecules. This electrostatic pressure has the same effect as the application of an external pressure, and the compressibility of water molecules is lowered leading to an increase in sound velocity. Also, the addition of lithium acetate and lithium chloride in water actually increases the fluidity of water molecules in the vicinity of these ions, which probably become more mobile than those in water. As temperature increases, more voids are produced, which resulted in more hydration, which in turn, increases cohesion and hence the velocity. Such an increase is observed in the present study also.

The adiabatic compressibility decreases as the concentration and temperature increases. This is because as the concentration of electrolytes increases, larger portions of the water molecules are electrostricted and amount of bulk water decreases causing the adiabatic compressibility to decrease [8,16]. Such a decrease in adiabatic compressibility is observed in the present study.

As temperatures of these aqueous electrolyte solutions are increased, there is no definite ultrasonic velocity maxima observed. This may be due to the fact that pure water shows a temperature velocity maximum at a temperature 348K. The addition of electrolytes, changes the temperature velocity maximum for pure water. The thermal energy disrupts the water clusters with addition of electrolytes, resulting in an increase of

dense monomer population and increased cohesion. The increased cohesion always results in an increase in ultrasonic velocity. Further, it can be inferred that as the temperature is increased, more voids are produced which increase the closed packed structure of water. This also leads to increased cohesion and the stabilization of the hydrogen-bonded structure of pure water against thermal collapses by the electrolytes. Such an increase is observed in the case of aqueous solutions of lithium acetate and lithium chloride also.

From this ultrasonic velocity study, it is inferred that acetate ions have a greater structure breaking effect than chloride ions.

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